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(54) Title: SUPPORT MATERIALS FOR USE WITH POLYMERIZATION CATALYSTS

(57) Abstract: The invention provides new polymerization catalyst systems, including polystyrene support materials, which pos-  
sesses higher activity when compared to those systems utilizing the same catalyst compound and activator supported on silica. The  
invention also provides methods of preparing the catalyst system, and to the catalyst system's use in a gas or slurry polymerization  
process.

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**SUPPORT MATERIALS FOR USE WITH POLYMERIZATION CATALYSTS****FIELD OF THE INVENTION**

**[0001]** The present invention relates generally to the field of new support materials for use with polymerization catalysts. In particular, the present invention is directed to new catalyst systems comprising a polystyrene support material and a polymerization catalyst compound, to methods for preparing these supported catalyst systems, and their use in the polymerization of olefin(s).

**BACKGROUND OF THE INVENTION**

**[0002]** Developments in polymerization technology have provided more efficient, highly productive and economically enhanced catalyst systems and processes. Especially illustrative of these advances is the development of bulky ligand metallocene catalysts and of Group 15 metal containing catalysts. To utilize these catalyst compounds in industrial slurry or gas phases processes, it is useful that they be immobilized on a support or carrier.

**[0003]** The use of supported or heterogeneous catalysts in gas and slurry phase polymerization is important as a means of increasing process efficiencies by assuring that the forming polymeric particles achieve shape and density that improves reactor operability and ease of handling. Ineffective catalyst supports permit the production of polymeric fines and fouling of reactor walls or piping. This appears to be due to a number of possible reasons, including premature support particle fragmentation or catalyst desorption, both of which can lead to decrease in the control of polymerization. Polymer particle size and density can be degraded and efficiencies lost.

**[0004]** Typical heterogeneous catalyst systems include inorganic oxide supports, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO. These inorganic oxide supports, which may be used in concert with a catalyst activator compound, are available in a variety of particle sizes and porosities. However, silica and other inorganic oxide supports have several deficiencies. For example, the presence of water on the surface of inorganic oxide supports is known in the art to be a catalyst poison adversely affecting catalyst activity. To remove water from the surface, inorganic oxide supports must be calcined at high temperatures or chemically

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treated with appropriate reagents. In addition, inorganic oxides also readily adsorb other commonly occurring catalyst poisons, such as oxygen.

**[0005]** Moreover, with the emergence of discrete single-sited catalysts, research has shown that the use of such supports leads to a great deterioration of catalyst activity, often leading to prohibitively high catalyst costs in commercial applications. Further, certain catalysts bearing reactive functionalities (e.g., newer metallocene-type catalysts and/or non-coordinating anions) are largely or entirely inactive when deposited on silica supports.

**[0006]** Where conventional Ziegler-Natta catalysts have been successfully prepared employing conventional silica (and other) support materials, experience continues to show that discrete metallocene and metallocene-type catalysts suffer significant activity losses when common supports are used. For catalysts that incorporate inexpensive precursors and display very high activities, such losses may be acceptable for commercial operation. However, for many catalysts, deterioration of catalytic activity through the use of conventional supporting materials can lead to prohibitively high catalyst costs, precluding their use from commercial applications. This is especially true for catalysts that possess metal to nitrogen and metal to oxygen bonds, or which employ non-coordinating anions for charge balance. It is likely that the activity losses observed upon supporting these catalysts arise from deleterious interactions of these sensitive species with Lewis basic and/or hydroxylic sites on the support.

**[0007]** Polymers can be used as catalyst supports since they are less susceptible to typical catalyst killing impurities such as, for example, water and oxygen. Porous polymer particles used as a support for metallocene catalysts are disclosed in, for example, U.S. Pat. No. 4,921,825, U.S. Pat. No. 5,051,484, U.S. Pat. No. 5,118,648, U.S. Pat. No. 5,362,824, U.S. Pat. No. 6,100,214 and U.S. Pat. No. 6,013,594.

**[0008]** A number of researchers have reported on the use of polymer supports for homogeneous catalysis (Sherrington, D. C. *J. Chem. Soc., Chem. Comm.* 1998, 2275-2286). In particular, olefin polymerization catalysts have received much attention from industry and academia alike as subjects for immobilization on polymeric supports (See for example: Abbenhuis, H. C. L. *Angew. Chem. Int. Ed. Engl.* 1999, 38, 1058-1060; Duchateau, R., van Santen, R. A., Yap, G. P. A. *Organometallics*. 1999, 19, 809-816; Hlatky, G. G. *Chem. Rev.* 2000, 100, 1347-1376; Hong, S. C., Teranishi, T., Soga, K.

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*Polymer* 1998, 39; Ohnishi, K., Mori, H., Terano, M., *Macromol. Chem. Phys.* 1998, 199, 1765-1770; and Roscoe, S. B., Frechet, J., Walzer, J. F., *Science* 1998, 280, 270-273.)

[0009] In much of this work on polymeric support for olefin polymerization, great effort was expended to attach the catalyst or activator compound to the support surface to prevent catalyst leaching, which can occur especially in a slurry-phase polymerization environment. In the present invention, polystyrene materials that lack functionality, which could interact with the catalyst, and that possess defined pore volumes and pore sizes were sought.

[0010] While these catalyst systems and methods have been described in the art, a need exists for improved catalyst systems utilizing new support materials, for methods of preparing catalyst systems utilizing new support materials and for a polymerization process utilizing such supported catalyst systems. It is therefore an object of this invention to identify support materials that preserve both the activity and the polymer properties of "unsupportable" catalysts in the sense of traditional support materials, that will perform in existing or minimally-modified commercial catalyst feeding configurations. It is also an object of this invention to use several simple and commercially-available materials as supports for catalysts for use in polyolefin polymerization environments where the catalysts activity in solution, which is usually greater than when the catalyst is supported, is retained.

### **SUMMARY OF THE INVENTION**

[0011] This invention provides a new catalyst system including polystyrene support materials that possesses higher activity compared to inorganic oxide supported catalyst systems utilizing the same catalyst compound and activator.

[0012] In one embodiment, the invention provides a catalyst system including a catalyst compound, an activator compound and a polystyrene support material, to methods of preparing the catalyst system, and to the catalyst system's use in a polymerization process.

### **DETAILED DESCRIPTION OF THE INVENTION**

#### **Introduction**

[0013] The catalyst compounds, that may be utilized with the polystyrene support material in the catalyst systems of invention, include bulky ligand metallocene catalyst compounds and Group 15 containing metal compounds.

**Bulky Ligand Metallocene Catalyst Compounds**

**[0014]** Polystyrene support materials may be utilized with the bulky ligand metallocene polymerization catalyst compounds described below. Generally, these catalyst compounds include half and full sandwich compounds having one or more bulky ligands bonded to at least one metal atom. Typical bulky ligand metallocene compounds are described as containing one or more bulky ligand(s) and one or more leaving group(s) bonded to at least one metal atom. In one preferred embodiment, at least one bulky ligands is  $\eta^5$ -bonded to the metal atom, most preferably  $\eta^5$ -bonded to a transition metal atom.

**[0015]** The bulky ligands are generally represented by one or more open, acyclic, or fused ring(s) or ring system(s) or a combination thereof. The ring(s) or ring system(s) of these bulky ligands are typically composed of atoms selected from Groups 13 to 16 atoms of the Periodic Table of Elements. Preferably the atoms are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum or a combination thereof. Most preferably the ring(s) or ring system(s) are composed of carbon atoms such as but not limited to those cyclopentadienyl ligands or cyclopentadienyl-type ligand structures or other similar functioning ligand structure such as a pentadiene, a cyclooctatetraendiyl or an imide ligand. The metal atom is preferably selected from Groups 3 through 15 and the lanthanide or actinide series of the Periodic Table of Elements. Preferably the metal is a transition metal from Groups 4 through 12, more preferably Groups 4, 5 and 6, and most preferably the transition metal is from Group 4.

**[0016]** In one embodiment, the polystyrene support materials may be utilized with the bulky ligand metallocene catalyst compounds represented by the formula:



where M is a metal atom from the Periodic Table of the Elements and may be a Group 3 to 12 metal or from the lanthanide or actinide series of the Periodic Table of Elements, preferably M is a Group 4, 5 or 6 transition metal, more preferably M is zirconium, hafnium or titanium. The bulky ligands,  $L^A$  and  $L^B$ , are open, acyclic or fused ring(s) or ring system(s) and are any ancillary ligand system, including unsubstituted or substituted,

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cyclopentadienyl ligands or cyclopentadienyl-type ligands, heteroatom substituted and/or heteroatom containing cyclopentadienyl-type ligands. Non-limiting examples of bulky ligands include cyclopentadienyl ligands, cyclopentaphenanthrenyl ligands, indenyl ligands, benzindenyl ligands, fluorenyl ligands, octahydrofluorenyl ligands,

- 5 cyclooctatetraendiyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, phosphinimine (WO 99/40125), pyrrolyl ligands, pyroazolyl ligands, carbazolyl ligands, borabenzene ligands and the like, including hydrogenated versions thereof, for example tetrahydroindenyl ligands. In one embodiment,  $L^A$  and  $L^B$  may be any other ligand structure capable of  $\eta$ -bonding to M, preferably  $\eta^3$ -
- 10 bonding to M and most preferably  $\eta^5$ -bonding. In yet another embodiment, the atomic molecular weight (MW) of  $L^A$  or  $L^B$  exceeds 60 a.m.u., preferably greater than 65 a.m.u.. In another embodiment,  $L^A$  and  $L^B$  may comprise one or more heteroatoms, for example, nitrogen, silicon, boron, germanium, sulfur and phosphorous, in combination with carbon atoms to form an open, acyclic, or preferably a fused, ring or ring system, for example, a
- 15 hetero-cyclopentadienyl ancillary ligand. Other  $L^A$  and  $L^B$  bulky ligands include but are not limited to bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borollides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles. Independently, each  $L^A$  and  $L^B$  may be the same or different type of bulky ligand that is bonded to M. In one embodiment of formula (I) only one of either  $L^A$  or  $L^B$  is present.

- 20 **[0017]** Independently, each  $L^A$  and  $L^B$  may be unsubstituted or substituted with a combination of substituent groups R. Non-limiting examples of substituent groups R include one or more from the group selected from hydrogen, or linear, branched alkyl radicals, or alkenyl radicals, alkynyl radicals, cycloalkyl radicals or aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino
- 25 radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbomoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. In a preferred embodiment, substituent groups R have up to 50 non-hydrogen atoms, preferably from 1 to 30 carbon, that can also be substituted with halogens or heteroatoms or the like. Non-
- 30 limiting examples of alkyl substituents R include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers,

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for example tertiary butyl, isopropyl, and the like. Other hydrocarbyl radicals include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl, chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)-silyl, methyl-bis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Non-hydrogen substituents R include the atoms carbon, silicon, boron, aluminum, nitrogen, phosphorous, oxygen, tin, sulfur, germanium and the like, including olefins such as but not limited to olefinically unsaturated substituents including vinyl-terminated ligands, for example but-3-enyl, prop-2-enyl, hex-5-enyl and the like. Also, at least two R groups, preferably two adjacent R groups, are joined to form a ring structure having from 3 to 30 atoms selected from carbon, nitrogen, oxygen, phosphorous, silicon, germanium, aluminum, boron or a combination thereof. Also, a substituent group R group such as 1-butan-1-yl may form a carbon sigma bond to the metal M.

**[0018]** Other ligands may be bonded to the metal M, such as at least one leaving group Q. For the purposes of this patent specification and appended claims the term “leaving group” is any ligand that can be abstracted from a bulky ligand metallocene catalyst compound to form a bulky ligand metallocene catalyst cation capable of polymerizing one or more olefin(s). In one embodiment, Q is a monoanionic labile ligand having a sigma-bond to M. Depending on the oxidation state of the metal, the value for n is 0, 1 or 2 such that formula (I) above represents a neutral bulky ligand metallocene catalyst compound.

**[0019]** Non-limiting examples of Q ligands include weak bases such as amines, phosphines, ethers, carboxylates, dienes, hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides or halogens and the like or a combination thereof. In another embodiment, two or more Q's form a part of a fused ring or ring system. Other examples of Q ligands include those substituents for R as described above and including cyclobutyl, cyclohexyl, heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methylenedioxy, methoxy,

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ethoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, dimethylphosphide radicals and the like.

**[0020]** In another embodiment, the polystyrene support materials may be utilized with the bulky ligand metallocene catalyst compounds of formula (I) where  $L^A$  and  $L^B$  are bridged to each other by at least one bridging group, A, as represented in the following formula:



**[0021]** These bridged compounds represented by formula (II) are known as bridged, bulky ligand metallocene catalyst compounds.  $L^A$ ,  $L^B$ , M, Q and n are as defined above. Non-limiting examples of bridging group A include bridging groups containing at least one Group 13 to 16 atom, often referred to as a divalent moiety such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom or a combination thereof. Preferably bridging group A contains a carbon, silicon or germanium atom, most preferably A contains at least one silicon atom or at least one carbon atom. The bridging group A may also contain substituent groups R as defined above including halogens and iron. Non-limiting examples of bridging group A may be represented by  $R'_2C$ ,  $R'_2Si$ ,  $R'_2Si R'_2Si$ ,  $R'_2Ge$ ,  $R'_2P$ , where  $R'$  is independently, a radical group which is hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen or two or more  $R'$  may be joined to form a ring or ring system. In one embodiment, the bridged, bulky ligand metallocene catalyst compounds of formula (II) have two or more bridging groups A (EP 664 301 B1).

**[0022]** In one embodiment, the bulky ligand metallocene catalyst compounds are those where the R substituents on the bulky ligands  $L^A$  and  $L^B$  of formulas (I) and (II) are substituted with the same or different number of substituents on each of the bulky ligands. In another embodiment, the bulky ligands  $L^A$  and  $L^B$  of formulas (I) and (II) are different from each other.

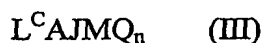


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**[0023]** Other bulky ligand metallocene catalyst compounds and catalyst systems useful in the invention may include those described in U.S. Patent Nos. 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031, 5,304,614, 5,677,401, 5,723,398, 5,753,578, 5,854,363, 5,856,547, 5,858,903, 5,859,158, 5,900,517 and 5,939,503 and PCT publications WO 93/08221, WO 93/08199, WO 95/07140, WO 98/11144, WO 98/41530, WO 98/41529, WO 98/46650, WO 99/02540 and WO 99/14221 and European publications EP-A-0 578 838, EP-A-0 638 595, EP-B-0 513 380, EP-A1-0 816 372, EP-A2-0 839 834, EP-B1-0 632 819, EP-B1-0 748 821 and EP-B1-0 757 996, all of which are herein fully incorporated by reference.

**[0024]** In one embodiment, bulky ligand metallocene catalysts compounds useful in the invention include bridged heteroatom, mono-bulky ligand metallocene compounds. These types of catalysts and catalyst systems are described in, for example, PCT publication WO 92/00333, WO 94/07928, WO 91/04257, WO 94/03506, WO96/00244, WO 97/15602 and WO 99/20637 and U.S. Patent Nos. 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440 and 5,264,405 and European publication EP-A-0 420 436, all of which are herein fully incorporated by reference.

**[0025]** In this embodiment, the bulky ligand metallocene catalyst compound is represented by the formula:



where M is a Group 3 to 16 metal atom or a metal selected from the Group of actinides and lanthanides of the Periodic Table of Elements, preferably M is a Group 4 to 12 transition metal, and more preferably M is a Group 4, 5 or 6 transition metal; and most preferably M is a Group 4 transition metal in any oxidation state, especially titanium;  $L^C$  is a substituted or unsubstituted bulky ligand bonded to M; J is bonded to M; A is bonded to  $L^C$  and J; J is a heteroatom ancillary ligand; and A is a bridging group; Q is a univalent anionic ligand; and n is the integer 0, 1 or 2. In formula (III) above,  $L^C$ , A and J form a fused ring system. In an embodiment,  $L^C$  of formula (III) is as defined above for  $L^A$ , A, M and Q of formula (I).

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**[0026]** In formula (III) J is a heteroatom containing ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of Elements. Preferably J contains a nitrogen, phosphorus, oxygen or sulfur atom with nitrogen being most preferred.

5 **[0027]** In another embodiment, the bulky ligand type metallocene catalyst compound is a complex of a metal, preferably a transition metal, a bulky ligand, preferably a substituted or unsubstituted pi-bonded ligand, and one or more heteroallyl moieties, such as those described in U.S. Patent Nos. 5,527,752 and 5,747,406 and EP-B1-0 735 057, all of which are herein fully incorporated by reference.

10 **[0028]** In an embodiment, the polystyrene support materials may be utilized with the bulky ligand metallocene catalyst compounds represented by the formula:



15 where M is a Group 3 to 16 metal, preferably a Group 4 to 12 transition metal, and most preferably a Group 4, 5 or 6 transition metal;  $L^D$  is a bulky ligand that is bonded to M; each Q is independently bonded to M and  $Q_2(YZ)$  forms a unicharged polydentate ligand; A or Q is a univalent anionic ligand also bonded to M; X is a univalent anionic group when n is 2 or X is a divalent anionic group when n is 1; n is  
20 1 or 2.

**[0029]** In formula (IV), L and M are as defined above for formula (I). Q is as defined above for formula (I), preferably Q is selected from the group consisting of -O-, -NR-, -CR<sub>2</sub>- and -S-; Y is either C or S; Z is selected from the group consisting of -OR, -NR<sub>2</sub>, -CR<sub>3</sub>, -SR, -SiR<sub>3</sub>, -PR<sub>2</sub>, -H, and substituted or unsubstituted aryl  
25 groups, with the proviso that when Q is -NR- then Z is selected from one of the group consisting of -OR, -NR<sub>2</sub>, -SR, -SiR<sub>3</sub>, -PR<sub>2</sub> and -H; R is selected from a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus, preferably where R is a hydrocarbon group containing from 1 to 20 carbon atoms, most preferably an alkyl, cycloalkyl, or an aryl group; n is an integer from 1 to 4, preferably 1 or 2; X is a  
30 univalent anionic group when n is 2 or X is a divalent anionic group when n is 1;

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preferably X is a carbamate, carboxylate, or other heteroallyl moiety described by the Q, Y and Z combination.

**[0030]** In another embodiment of the invention, the bulky ligand metallocene-type catalyst compounds are heterocyclic ligand complexes where the bulky ligands, the ring(s) or ring system(s), include one or more heteroatoms or a combination thereof. Non-limiting examples of heteroatoms include a Group 13 to 16 element, preferably nitrogen, boron, sulfur, oxygen, aluminum, silicon, phosphorous and tin. Examples of these bulky ligand metallocene catalyst compounds are described in WO 96/33202, WO 96/34021, WO 97/17379 and WO 98/22486 and EP-A1-0 874 005 and U.S. Patent No. 5,637,660, 5,539,124, 5,554,775, 5,756,611, 5,233,049, 5,744,417, and 5,856,258 all of which are herein incorporated by reference.

**[0031]** In another embodiment, the bulky ligand metallocene catalyst compounds are those complexes known as transition metal catalysts based on bidentate ligands containing pyridine or quinoline moieties, such as those described in U.S. Application Serial No. 09/103,620 filed June 23, 1998, which is herein incorporated by reference. In another embodiment, the bulky ligand metallocene catalyst compounds are those described in PCT publications WO 99/01481 and WO 98/42664, which are fully incorporated herein by reference.

**[0032]** In one embodiment, the polystyrene support materials may be utilized with the bulky ligand metallocene catalyst compounds represented by the formula:



where M is a metal selected from Group 3 to 13 or lanthanide and actinide series of the Periodic Table of Elements; Q is bonded to M and each Q is a monovalent, bivalent, or trivalent anion; X and Y are bonded to M; one or more of X and Y are heteroatoms, preferably both X and Y are heteroatoms; Y is contained in a heterocyclic ring J, where J comprises from 2 to 50 non-hydrogen atoms, preferably 2 to 30 carbon atoms; Z is bonded to X, where Z comprises 1 to 50 non-hydrogen atoms, preferably 1 to 50 carbon atoms, preferably Z is a cyclic group containing 3 to 50 atoms, preferably 3 to 30 carbon atoms; t is 0 or 1; when t is 1, A is a bridging group joined to at least one of X, Y or J,

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preferably X and J; q is 1 or 2; n is an integer from 1 to 4 depending on the oxidation state of M. In one embodiment, where X is oxygen or sulfur then Z is optional. In another embodiment, where X is nitrogen or phosphorous then Z is present. In an embodiment, Z is preferably an aryl group, more preferably a substituted aryl group.

5 **[0033]** It is also within the scope of this invention, in one embodiment, that the bulky ligand metallocene catalyst compounds include complexes of  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$  described in the articles Johnson, et al., "New Pd(II)- and Ni(II)- Based Catalysts for Polymerization of Ethylene and  $\alpha$ -Olefins", J. Am. Chem. Soc. 1995, 117, 6414-6415 and Johnson, et al., "Copolymerization of Ethylene and Propylene with Functionalized  
10 Vinyl Monomers by Palladium(II) Catalysts", J. Am. Chem. Soc., 1996, 118, 267-268, and WO 96/23010 published August 1, 1996, WO 99/02472, U.S. Patent Nos. 5,852,145, 5,866,663 and 5,880,241, which are all herein fully incorporated by reference. These complexes can be either dialkyl ether adducts, or alkylated reaction products of the described dihalide complexes that can be activated to a cationic state by  
15 the activators of this invention described below.

**[0034]** Also included as bulky ligand metallocene catalyst are those diimine based ligands of Group 8 to 10 metal compounds disclosed in PCT publications WO 96/23010 and WO 97/48735 and Gibson, et. al., Chem. Comm., pp. 849-850 (1998), all of which are herein incorporated by reference.

20 **[0035]** Other bulky ligand metallocene catalysts are those Group 5 and 6 metal imido complexes described in EP-A2-0 816 384 and U.S. Patent No. 5,851,945, which is incorporated herein by reference. In addition, bulky ligand metallocene catalysts include bridged bis(arylamido) Group 4 compounds described by D.H. McConville, et al., in Organometallics 1195, 14, 5478-5480, which is herein incorporated by reference.  
25 In addition, bridged bis(amido) catalyst compounds are described in WO 96/27439, which is herein incorporated by reference. Other bulky ligand metallocene catalysts are described as bis(hydroxy aromatic nitrogen ligands) in U.S. Patent No. 5,852,146, which is incorporated herein by reference. Other metallocene catalysts containing one or more Group 15 atoms include those described in WO 98/46651, which is herein  
30 incorporated herein by reference. Still another metallocene bulky ligand metallocene

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catalysts include those multinuclear bulky ligand metallocene catalysts as described in WO 99/20665, which is incorporated herein by reference.

**[0036]** It is also contemplated that in one embodiment, the bulky ligand metallocene catalysts of the invention described above include their structural or optical enantiomeric isomers (meso and racemic isomers, for example see U.S. Patent No. 5,852,143, incorporated herein by reference) and mixtures thereof.

### **Group 15 Containing Polymerization Catalyst**

**[0037]** The polystyrene support materials may be utilized with Group 15 metal containing polymerization catalyst. Generally, these catalysts includes a Group 3 to 14 metal atom, preferably a Group 3 to 7, more preferably a Group 4 to 6, and even more preferably a Group 4 metal atom, bound to at least one leaving group and also bound to at least two Group 15 atoms, at least one of which is also bound to a Group 15 or 16 atom through another group.

**[0038]** Preferably, at least one of the Group 15 atoms is also bound to a Group 15 or 16 atom through another group which may be a C<sub>1</sub> to C<sub>20</sub> hydrocarbon group, a heteroatom containing group, silicon, germanium, tin, lead, or phosphorus, wherein the Group 15 or 16 atom may also be bound to nothing or a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group, and wherein each of the two Group 15 atoms are also bound to a cyclic group and may optionally be bound to hydrogen, a halogen, a heteroatom or a hydrocarbyl group, or a heteroatom containing group.

**[0039]** It is also contemplated that any one of the catalyst compounds described above may have at least one fluoride or fluorine containing leaving group as described in U.S. Application Serial No. 09/191,916 filed November 13, 1998.

**[0040]** In another embodiment of the invention the composition containing alternating atoms of Group 14 and Group 16 may be used to create solutions or emulsions including one or more bulky ligand metallocene catalyst compounds, and one or more conventional-type catalyst compounds or catalyst systems. Non-limiting examples of mixed catalysts and catalyst systems are described in U.S. Patent Nos. 4,159,965, 4,325,837, 4,701,432, 5,124,418, 5,077,255, 5,183,867, 5,391,660, 5,395,810, 5,691,264, 5,723,399

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and 5,767,031 and PCT Publication WO 96/23010 published August 1, 1996, all of which are herein fully incorporated by reference.

### **Activator Compositions**

5   **[0041]**       The above described polymerization catalyst compounds are typically activated in various ways to yield compounds having a vacant coordination site that will coordinate, insert, and polymerize olefin(s). The catalyst system of the invention may include an activator or activators combined with the polystyrene support materials.

10   **[0042]**       For the purposes of this patent specification and appended claims, the term "activator" is defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst compound cation. Non-limiting activators, for example, include alumoxanes, aluminum alkyls, and ionizing activators, which may be neutral or ionic.

15   **[0043]**       In one embodiment, alumoxanes activators are utilized as an activator in the catalyst composition of the invention. Alumoxanes are generally oligomeric compounds containing -Al(R)-O- subunits, where R is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alumoxanes may be produced by the hydrolysis of the respective trialkylaluminum compound. MMAO may be produced by the hydrolysis of  
20   trimethylaluminum and a higher trialkylaluminum such as triisobutylaluminum. MMAO's are generally more soluble in aliphatic solvents and more stable during storage. There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032,  
25   5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253, 5,731,451, 5,744,656, 5,847,177, 5,854,166, 5,856,256 and 5,939,346 and European publications EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and EP-B1-0 586 665, and PCT publications WO 94/10180 and WO 99/15534, all of which are herein fully incorporated by reference. A another alumoxane is a modified methyl alumoxane (MMAO)  
30   cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number US 5,041,584).

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**[0044]** Aluminum alkyl or organoaluminum compounds that may be utilized as activators include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like.

**[0045]** In another embodiment, the catalyst system of the invention includes an ionizing or stoichiometric activator, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) boron, a trisperfluorophenyl boron metalloid precursor or a trisperfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Patent No. 5,942,459) or combination thereof. It is also within the scope of this invention to use neutral or ionic activators alone or in combination with alumoxane or modified alumoxane activators.

**[0046]** Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium and indium or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogen, substituted alkyls, aryls, arylhalides, alkoxy and halides. Preferably, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds and mixtures thereof, preferred are alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls). More preferably, the three groups are alkyls having 1 to 4 carbon groups, phenyl, naphthyl or mixtures thereof. Even more preferably, the three groups are halogenated, preferably fluorinated, aryl groups. Most preferably, the neutral stoichiometric activator is trisperfluorophenyl boron or trisperfluoronaphthyl boron.

**[0047]** Ionic stoichiometric activator compounds may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-B1-0 500 944, EP-A-0 277 003 and EP-A-0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299 and 5,502,124 and U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994, all of which are herein fully incorporated by reference.

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**[0048]** In another embodiment, the stoichiometric activators include a cation and an anion component, and may be represented by the following formula:



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wherein L is an neutral Lewis base;

H is hydrogen;

$(L-H)^+$  is a Bronsted acid

$A^{d-}$  is a non-coordinating anion having the charge d-

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d is an integer from 1 to 3.

**[0049]** The cation component,  $(L-H)_d^+$  may include Bronsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating or abstracting a moiety, such as an alkyl or aryl, from the bulky ligand metallocene or Group 15 containing transition metal catalyst precursor, resulting in a cationic transition metal species.

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**[0050]** The activating cation  $(L-H)_d^+$  may be a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums and mixtures thereof, preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene and mixtures thereof. The activating cation  $(L-H)_d^+$  may also be an abstracting moiety such as silver, carboniums, tropylium, carbeniums, ferroceniums and mixtures, preferably carboniums and ferroceniums. Most preferably  $(L-H)_d^+$  is triphenyl carbonium.

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**[0051]** The anion component  $A^{d-}$  include those having the formula  $[M^{k+}Q_n]^{d-}$  wherein k is an integer from 1 to 3; n is an integer from 2-6; n - k = d; M is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or



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aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluorophenyl group. Examples of suitable  $A^{d-}$  also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

5 **[0052]** In a most preferred embodiment, the ionic stoichiometric activator  $(L-H)_d^+$  ( $A^{d-}$ ) is N,N-dimethylanilinium tetra(perfluorophenyl)borate or triphenylcarbenium tetra(perfluorophenyl)borate.

**[0053]** Examples of suitable  $A^{d-}$  also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

15 **[0054]** In one embodiment, an activation method using ionizing ionic compounds not containing an active proton but capable of producing a Group 15 containing metal compound cation or bulky ligand metallocene catalyst cation and their non-coordinating anion are also contemplated, and are described in EP-A- 0 426 637, EP-A- 0 573 403 and U.S. Patent No. 5,387,568, which are all herein incorporated by reference.

20 **[0055]** Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2''- nonafluorobiphenyl) fluoroaluminate, which publication is fully incorporated herein by reference. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP-B1 0 573 120, PCT publications WO 94/07928 and WO 95/14044 and U.S. Patent Nos. 5,153,157 and 5,453,410 all of which are herein fully incorporated by reference.

25 **[0056]** Other suitable activators are disclosed in WO 98/09996, incorporated herein by reference, which describes activating bulky ligand metallocene catalyst compounds with perchlorates, periodates and iodates including their hydrates. WO 98/30602 and WO 98/30603, incorporated by reference, describe the use of lithium (2,2'-bisphenyl-ditrimethylsilicate)•4THF as an activator for a bulky ligand metallocene catalyst compound.  
30 WO 99/18135, incorporated herein by reference, describes the use of organo-boron-aluminum activators. EP-B1-0 781 299 describes using a silylium salt in combination with

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a non-coordinating compatible anion. Also, methods of activation such as using radiation (see EP-B1-0 615 981 herein incorporated by reference), electro-chemical oxidation, and the like are also contemplated as activating methods for the purposes of rendering the neutral bulky ligand metallocene catalyst compound or precursor to a bulky ligand metallocene cation capable of polymerizing olefins. Other activators or methods for activating a bulky ligand metallocene catalyst compound are described in for example, U.S. Patent Nos. 5,849,852, 5,859,653 and 5,869,723 and WO 98/32775, WO 99/42467 (dioctadecylmethylammonium-bis(tris(pentafluorophenyl)borane) benzimidazolidine), which are herein incorporated by reference.

### Polystyrene Support Materials

**[0057]** The catalyst system of the invention includes a polystyrene support material. Typically, catalyst compounds and/or activator compounds are deposited on, contacted with, vaporized with, bonded to, or incorporated within, adsorbed or absorbed in, or on, a support or carrier. Functionality on the outer surface and on the surface of the support pores, however, can interact deleteriously with the activated catalyst site to cause a reduction in catalytic activity. The polystyrene supports used in this invention are selected such that these interactions will be minimized.

**[0058]** A support with an "inert surface" is one without surface functionality that will chemically interact with a catalyst compound and/or an activator compound. In other words, the surface lacks functional groups such as -OH, strained Si-O-Si, -NH<sub>2</sub>, -SH and alkenes that will be reactive towards organic ligands. By the term inert surface, it is not meant to imply that there are no chemical binding interactions at the surface. At the molecular level, all surfaces contain defects and morphological characteristics that give rise to some interactions.

**[0059]** In one embodiment, the polystyrene support material has a surface area in the range of from about 10 to about 700 m<sup>2</sup>/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 μm. More preferably, the surface area of the support material is in the range of from about 50 to about 500 m<sup>2</sup>/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 μm. Most preferably the surface area of the support material is in the

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range is from about 100 to about 400 m<sup>2</sup>/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 5 to about 100 μm. The average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000 Å, preferably 50 to about 500 Å, and most preferably 75 to about 350 Å.

5   **[0060]**       In one embodiment in a method to form a supported catalyst compound and/or activator compound, the amount of liquid in which the catalyst and/or activator is present is in an amount that is less than four times the pore volume of the support material, more preferably less than three times, even more preferably less than two times; preferred ranges being from 1.1 times to 3.5 times range and most preferably in the 1.2 to 3 times  
10   range. In an alternative embodiment, the amount of liquid in which the activator is present is from one to less than one times the pore volume of the support material utilized in forming the supported activator.

**[0061]**       Procedures for measuring the total pore volume of a porous support are well known in the art. Details of one of these procedures is discussed in Volume 1,  
15   *Experimental Methods in Catalytic Research* (Academic Press, 1968) (specifically see pages 67-96). This preferred procedure involves the use of a classical BET apparatus for nitrogen absorption. Another method well known in the art is described in Innes, *Total Porosity and Particle Density of Fluid Catalysts By Liquid Titration*, Vol. 28, No. 3, Analytical Chemistry 332-334 (March, 1956).

20   **[0062]**       In one embodiment, the polystyrene support materials have a high melting point, and are relatively insoluble under polymerization reactor conditions. In another embodiment, the polystyrene support materials are copolymerized with divinyl benzene. Preferably, the polystyrene support materials of the invention are lightly cross-linked with divinyl benzene, more preferably the polystyrene is >3% cross-linked, more preferably  
25   greater than 5% cross-linked, and even more preferably the polystyrene is about 5% cross-linked.

**[0063]**       In one embodiment, the physical properties of the polystyrene support material are controlled as is known in the art. (See for example: Wang *et al. J. Poly. Sci. Part A: Polymer Chem.* 1994, 32, 2577-2588, 1994; Lewandowski *et al. J. Appl. Poly. Sci.*  
30   1998, 67, 597-607, 1998; and Galia *et al., J. Poly Sci. Part A: Polymer Chem* 1994, 32, 2169-2175.) In one embodiment, porogens are utilized to control the pore volume. In

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another embodiment, suspension polymerization is utilized to yield polystyrene having a spherical particle shape of controlled size.

**[0064]** In one embodiment, the polystyrene support material is simple crosslinked polystyrene materials such as Amberchrom and Diaion resins, both of which can be purchased from Supelco, Inc, Bellefonte, PA, as wet-packed beads, which are preferably dried and purified before use with polymerization catalysts. The properties of Amberchrom and Diaion are shown below in Table 1. In one embodiment, removal of the polystyrene initiator is effected according to the procedure developed by Lewandowski, K. et al. *J. Appl. Poly. Sci.* 1998, 67, 597-607. In another embodiment, the drying of the polystyrene support material is done in a vacuum oven operated at 75 °C. In another embodiment, the resins can be further dried by suspension in a pentane-TIBA (triisobutylaluminum) mixture, followed by filtration and drying under high vacuum.

**Table 1:** Properties of Amberchrom and Diaion polystyrene bead supports

Properties	Amberchrom	Diaion
Type	HP20SS	CG-300s
Particle Size (μm)	75-150	20-50
Pore Volume (mL/g)	1.3	1.66
Pore Diameter (Å)	300-600	300
Surface Area (m <sup>2</sup> /g)	500	700

**[0065]** Some catalyst compounds are more affected than others in terms of activity when supported. For example, in one embodiment, half-sandwich complex supported on polystyrene beads had a high polymerization activity when a borate was used as an activator, but low polymerization activity when alumoxane was used. In one embodiment, when higher polymerization activity or more polymer product is obtained, it is preferred that the catalytic activity on the new support material will be at least 1.2 times of the catalytic activity of the same catalysts on silica. It is more preferred that the catalytic

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activity will be at least 2, more preferably even greater than 3 times that of the catalytic activity of the same catalysts on silica.

### **Polymerization Process**

5    **[0066]**       The catalyst systems of the invention described above are suitable for use in any prepolymerization and/or polymerization process over a wide range of temperatures and pressures. The temperatures may be in the range of from -60 °C to about 280°C, preferably from 50°C to about 200°C, and the pressures employed may be in the range from 1 atmosphere to about 500 atmospheres or higher.

10   **[0067]**       Polymerization processes include solution, gas phase, slurry phase and a high pressure process or a combination thereof. Preferred is a gas phase or slurry phase polymerization of one or more olefins at least one of which is ethylene or propylene.

15   **[0068]**       In one embodiment, the process of this invention is directed toward a solution, high pressure, slurry or gas phase polymerization process of one or more olefin monomers having from 2 to 30 carbon atoms, preferably 2 to 12 carbon atoms, and more preferably 2 to 8 carbon atoms. The invention is particularly well suited to the polymerization of two or more olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1 and decene-1.

20   **[0069]**       Other monomers useful in the polymerization process of the invention include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene.

25   **[0070]**       In the most preferred embodiment of the process of the invention, a copolymer of ethylene is produced, where with ethylene, a comonomer having at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, and most preferably from 4 to 8 carbon atoms, is polymerized in a polymerization process.

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**[0071]** In another embodiment of the process of the invention, ethylene or propylene is polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

**[0072]** In one embodiment, the invention is directed to a polymerization process for polymerizing propylene alone or with one or more other monomers including ethylene, and/or other olefins having from 4 to 12 carbon atoms. Polypropylene polymers may be produced using the particularly bridged bulky ligand metallocene catalysts as described in U.S. Patent Nos. 5,296,434 and 5,278,264, both of which are herein incorporated by reference.

**[0073]** Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228, all of which are fully incorporated herein by reference.)

**[0074]** The reactor pressure in a gas phase process may vary from about 100 psig (690 kPa) to about 500 psig (3448 kPa), preferably in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), more preferably in the range of from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

**[0075]** The reactor temperature in a gas phase process may vary from about 30°C to about 120°C, preferably from about 60°C to about 115°C, more preferably in the range of from about 70°C to 110°C, and most preferably in the range of from about 70°C to about 95 °C.

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**[0076]** Other gas phase processes contemplated by the process of the invention include series or multistage polymerization processes. Also gas phase processes contemplated by the invention include those described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200 EP-B1-0 649 992, EP-A- 0 802 202 and EP-B- 634 421 all of which are herein fully incorporated by reference.

**[0077]** In a preferred embodiment, the reactor utilized in the present invention is capable and the process of the invention is producing greater than 500 lbs of polymer per hour (227 Kg/hr) to about 200,000 lbs/hr (90,900 Kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater than 35,000 lbs/hr (15,900 Kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

**[0078]** A slurry polymerization process generally uses pressures in the range of from about 1 to about 50 atmospheres and even greater and temperatures in the range of 0°C to about 120°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

**[0079]** A preferred polymerization technique of the invention is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Patent No. 3,248,179 which is fully incorporated herein by reference. Other slurry processes include those employing a loop reactor and

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those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Patent No. 4,613,484, which is herein fully incorporated by reference.

5   **[0080]**       In an embodiment the reactor used in the slurry process of the invention is capable of and the process of the invention is producing greater than 2000 lbs of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs/hr (2268 Kg/hr), and most preferably greater than 10,000 lbs/hr (4540 Kg/hr). In another embodiment the slurry reactor used in the process of the invention is producing greater than 15,000 lbs of polymer  
10 per hour (6804 Kg/hr), preferably greater than 25,000 lbs/hr (11,340 Kg/hr) to about 100,000 lbs/hr (45,500 Kg/hr).

**[0081]**       Examples of solution processes, where the siloxane catalyst and/or activator solutions or emulsions of the invention may be utilized, are described in U.S. Patent Nos. 4,271,060, 5,001,205, 5,236,998 and 5,589,555, which are fully incorporated herein by  
15 reference.

**[0082]**       A preferred process of the invention is where the process is operated in the presence of a bulky ligand metallocene catalyst system of the invention and in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminum, triisobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride, dibutyl zinc  
20 and the like. This preferred process is described in PCT publication WO 96/08520 and U.S. Patent No. 5,712,352 and 5,763,543, which are herein fully incorporated by reference.

**[0083]**       In one embodiment of the invention, olefin(s), preferably C<sub>2</sub> to C<sub>30</sub> olefin(s) or alpha-olefin(s), preferably ethylene or propylene or combinations thereof are prepolymerized in the presence of the catalyst solution or emulsion of the invention prior to  
25 the main polymerization. The prepolymerization can be carried out batchwise or continuously in gas, solution or slurry phase including at elevated pressures. The prepolymerization can take place with any olefin monomer or combination and/or in the presence of any molecular weight controlling agent such as hydrogen. For examples of prepolymerization procedures, see U.S. Patent Nos. 4,748,221, 4,789,359, 4,923,833,  
30 4,921,825, 5,283,278 and 5,705,578 and European publication EP-B-0279 863 and PCT Publication WO 97/44371 all of which are herein fully incorporated by reference.



**Polymer Products**

**[0084]** The polymers produced by the process of the invention can be used in a wide variety of products and end-use applications. The polymers produced by the process of the invention include linear low density polyethylene, elastomers, plastomers, high density polyethylenes, medium density polyethylenes, low density polyethylenes, polypropylene and polypropylene copolymers.

**[0085]** The polymers, typically ethylene based polymers, have a density in the range of from 0.86g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.96 g/cc, even more preferably in the range of from 0.905 g/cc to 0.95 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.940 g/cc, and most preferably greater than 0.915 g/cc, preferably greater than 0.920 g/cc, and most preferably greater than 0.925 g/cc. Density is measured in accordance with ASTM-D-1238.

**[0086]** The polymers produced by the process of the invention typically have a molecular weight distribution, a weight average molecular weight to number average molecular weight ( $M_w/M_n$ ) of greater than 1 to about 40, preferably greater than 1.5 to about 15, more preferably greater than 2 to about 10, most preferably greater than about 2.0 to about 8.

**[0087]** Also, the polymers of the invention typically have a narrow composition distribution as measured by Composition Distribution Breadth Index (CDBI). Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993, which is fully incorporated herein by reference.

**[0088]** The bulky ligand metallocene catalyzed polymers of the invention in one embodiment have CDBI's generally in the range of greater than 50% to 100%, preferably 99%, preferably in the range of 55% to 85%, and more preferably 60% to 80%, even more preferably greater than 60%, still even more preferably greater than 65%.

**[0089]** In another embodiment, polymers produced using a bulky ligand metallocene catalyst system of the invention have a CDBI less than 50%, more preferably less than 40%, and most preferably less than 30%.

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**[0090]** The polymers of the present invention in one embodiment have a melt index (MI) or ( $I_2$ ) as measured by ASTM-D-1238-E in the range of from less than 0.01 dg/min to 1000 dg/min, more preferably from about less than 0.01 dg/min to about 100 dg/min, even more preferably from about 0.1 dg/min to about 50 dg/min, and most preferably from about 0.1 dg/min to about 10 dg/min.

**[0091]** The polymers of the invention in an embodiment have a melt index ratio ( $I_{21}/I_2$ ) ( $I_{21}$  is measured by ASTM-D-1238-F) of about 5 to less than about 2500, preferably about 15 to about 250, more preferably about 10 to about 25, more preferably from about 15 to about 25.

**[0092]** The polymers of the invention in a preferred embodiment have a melt index ratio ( $I_{21}/I_2$ ) ( $I_{21}$  is measured by ASTM-D-1238-F) of from preferably greater than 10, more preferably greater than 30, even more preferably greater than 40, still even more preferably greater than 50 and most preferably greater than 65. In an embodiment, the polymer of the invention may have a narrow molecular weight distribution and a broad composition distribution or vice-versa, and may be those polymers described in U.S. Patent No. 5,798,427 incorporated herein by reference.

**[0093]** In yet another embodiment, propylene based polymers are produced in the process of the invention. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene polymers include propylene block or impact copolymers. Propylene polymers of these types are well known in the art see for example U.S. Patent Nos. 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117, all of which are herein incorporated by reference.

**[0094]** The polymers of the invention may be blended and/or coextruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylenes produced via conventional Ziegler-Natta and/or bulky ligand metallocene catalysis, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, polypropylenes and the like.

**[0095]** Polymers produced by the process of the invention and blends thereof are useful in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film,

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sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper  
5 fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, geomembranes, and pond liners. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

## 10 **EXAMPLES**

**[0096]** In order to provide a better understanding of the catalyst systems of the present invention including representative advantages thereof, the following examples are offered.

### **Definintions**

15 **[0097]** The term, "on the surface" of a support as used herein means that the catalyst compound and/or activator is at either the outer surface or inside the porous support material and/or interacting with the surface of the support through electrostatic interactions.

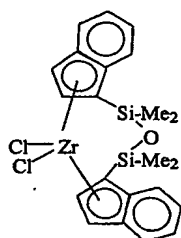
**[0098]** Solvents in which the catalyst system of the invention are formed can include but are not limited to: alkanes such as pentane, iso-pentane, hexane, heptane, octane, and  
20 nonane; cycloalkanes such as cyclopentane and cyclohexanes; aromatics such as benzene, toluene, ethylbenzene, and diethylbenzene; and halogen-containing solvents, such as methylene chloride and dichloromethane.

**[0099]** One of ordinary skill in the art will recognize the use of the phrase "substantially uniform" is meant to exclude wide variations in sizes, while allowing  
25 statistical variations, i.e. having a standard deviation of less than about 20%.

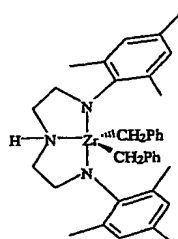
**[0100]** The activity of the catalyst system of the invention is compared to that utilizing the same catalyst compound on a silica support material. A silica supported catalyst system is a catalyst system supported on a silica, such as Davisson 958, purchased From Davisson, Columbia, MA. The preparation of this catalyst system is described in  
30 Comparative Example 16.

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**[0101]** As used herein, MAO is methylalumoxane, MMAO is modified methylaluminoxane. Cp is cyclopentadiene and Me is methyl. TIBA is triisobutylaluminum,  $(\text{Ind})_2\text{ZrCl}_2$  is bis(indenyl)zirconium dichloride. Catalyst A and B, referenced in the examples, are pictured below.



(Catalyst A)



(Catalyst B)

### **Example 1**

#### **General Procedures**

**[0102]** All manipulations were carried out in a glove box containing prepurified nitrogen or by using standard schlenk techniques. All solvents were purified by passing through a series of reduced copper chromite and activated alumina beds. Amberchrom and Diaion supports were purchased from Supelco, Inc, Bellefonte, PA. Controlled pore glasses were obtained from CPG, Inc., Lincoln Park, NJ. Graphite and polytetra-fluoroethylene (PTFE) were obtained from Aldrich Chemical, Milwaukee, WI. All support materials (except Davison 958 silica) were stirred in 1M triisobutylaluminum solution in pentane for at least 24 hrs, filtered and dried *in vacuo* prior to catalyst deposition. Methylaluminoxane (MAO) and modified methylaluminoxane (MMAO) were purchased from Akzo Nobel, Houston, TX. Triisobutylaluminum was purchased from Aldrich Chemical. All catalysts were prepared from previously published procedures well known in the art or purchased from Albemarle Corporation, Baton Rouge, LA.

#### **Slurry-Phase Ethylene Polymerization Experiments**

**[0103]** The following are procedures currently in use for testing various catalysts in the slurry phase. The basic reactor system consists of a one-liter stainless steel reactor vessel. A purge/evacuation cycle is initiated and the reactor is heated to 95°C with nitrogen flowing through the reactor at 500 sccm. Once the reactor has reached 95°C, three evacuation-refill cycles are carried out with dry nitrogen. After these cycles, the reactor is

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cooled to 60°C under a dry nitrogen purge at 200 sccm. When the reactor has reached a temperature below 60°C, 600 mL of hexane is charged to the reactor through a series of purification beds containing a reduced copper chromite catalyst, 13X molecular sieves and alumina. Once the hexane charge is completed, 1-hexene (43 mL, dried over 13X molecular sieves) and scavenging solution are added consecutively to the reactor through a reactor port. The scavenging solutions used for these experiments were modified methyl aluminoxane (MMAO, 250 equivalents, Type 3A, 1.84 M) and tri-isobutyl aluminum (TIBA, 200 equivalents). The reactor is then heated to 55°C for at least 10 minutes and is subsequently pressurized with ethylene to the set ethylene partial pressure (85 to 130 psi) (586 to 896 Kpa). The catalyst solution is then charged to the reactor via a pressurized bomb. Polymerization experiments are carried out for periods typically in the 30 to 40 minute range. Polymerization activities are determined from the weight of dried polymer recovered from slurry-phase experiments.

#### **Stirred-Bed Gas-Phase Ethylene Polymerization Experiments**

15 **[0104]** The following are the procedures currently in use for testing various catalysts in the gas-phase. The basic system consists of a one liter stainless steel reactor. To set up an experiment for a gas-phase run, a dip tube connector must be attached to a reactor port before starting the purge/heat cycle. A glass separatory funnel and injector bomb are taken into the glove box under nitrogen pressure. A sample (100 gram) of DSX-20 4810H polyethylene (starter bed) is weighed into the funnel. After a nitrogen purge cycle, the starter bed is charged to the reactor and three nitrogen purge/evacuation cycles are carried out at 1 minute intervals followed by three ethylene purge/evacuation cycles. When the ethylene purge-evacuation cycles are completed, a 1.00 mL sample of tri-isobutyl aluminum (1000  $\mu$ mol) scavenging solution (25% TIBA in hexane) is added to the reactor. 25 The bed is stirred for approximately 10 minutes while the reactor is pressurized with ethylene and brought to the run temperature. The catalyst is injected into the reactor by means of a pressurized bomb injection. Catalyst activities are determined from the volume of ethylene fed as measured by calibrated Brooks mass-flow controllers.

#### **Purification of commercial polystyrene beads**

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**[0105]** Polystyrene beads were purified according to the procedure of Frechet, J. et. al. *Science* 1998, 280, 270-273. Potassium carbonate (250 g) was weighed into a 1L beaker and dissolved with vigorous stirring in 500 mL of distilled water. Diaion HP-20SS resin or Amberchrom CG300s resin (200g) was weighed into a 2L beaker and slurried in the potassium carbonate solution. The slurry was stirred for 30 minutes and was filtered and washed with distilled water (300 mL). Concentrated hydrochloric acid (150 mL) was then added to 500 mL of water in a 1L beaker, combined with the resin in a 2 L beaker and then stirred for 30 minutes. The suspension was filtered and washed with distilled water (500 mL). The resin was then stirred in a 2L beaker with distilled water (500 mL) for 30 minutes.. After filtering, the resin was stirred with 600 mL methanol in a 2 L beaker for a period of 30 minutes. The resin was again filtered and washed with 200 mL fresh methanol and transferred to a clean beaker containing a fresh mixture of methanol and methylene chloride (250 mL methanol/75 mL methylene chloride). The suspension was stirred for 30 minutes. After filtration and washing with fresh methanol (100 mL), the resin was transferred to a 2L beaker containing a mixture of methanol and methylene chloride (120 mL methanol/980 mL methylene chloride). The suspension was stirred for 30 minutes. The suspension was again filtered and was washed with 100 mL of methylene chloride. The resin was stirred in 1500 mL of methylene chloride for a period of 30 minutes and was filtered and transferred to a clean 2L beaker. The resin was then stirred in a mixture of methanol and methylene chloride (300 mL methanol, 900 mL methylene chloride) for 30 minutes. After filtration, the resin was transferred to a 2L beaker and 1000 mL of methanol was added. The suspension was stirred for 30 minutes. The suspension was then filtered and washed with 100 mL of fresh methanol. The resin was then transferred into a 1L round bottom flask and vacuum dried on a schlenk line overnight.

### Comparative Example 2

#### Slurry-Phase Ethylene-1-Hexene Copolymerization by (Ind)<sub>2</sub>ZrCl<sub>2</sub>

**[0106]** A catalyst solution was prepared by dissolving solid (Ind)<sub>2</sub>ZrCl<sub>2</sub> (5.0 milligrams, 12.7  $\mu$ mol) in toluene (2.00 mL) and modified methyl aluminoxane (1.10 mL, 150  $\mu$ mol, 1.92 M). The catalyst mixture was stirred for 30 minutes. A 100  $\mu$ L aliquot

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(0.86  $\mu\text{mol}$ ) was loaded into the sample portion of the bomb. The catalyst solution was injected into the 1 liter autoclave reactor via the pressurized bomb.

### Example 3

5 Slurry-Phase Ethylene-1-Hexene Copolymerization by  $(\text{Ind})_2\text{ZrCl}_2$  on Amberchrome Polystyrene

[0107] A catalyst solution was prepared by dissolving  $(\text{Ind})_2\text{ZrCl}_2$  (3.37 milligrams, 8.6  $\mu\text{mol}$ ) in a solution of methyl aluminoxane (1.0 mL, type 3A, 13.1 wt.% Al and 4.27M). The catalyst mixture was stirred for 30 minutes. A 100  $\mu\text{mol}$  aliquot (0.86  $\mu\text{mol}$ ) was  
10 loaded onto Amberchrome support (100 mg). The loaded catalyst was shaken until the catalyst became a free flowing solid. All of the catalyst mixture was placed into the bomb and injected into the 1 liter autoclave

### Example 4

15 Slurry-Phase Ethylene-1-Hexene Copolymerization by  $(\text{Ind})_2\text{ZrCl}_2$  on Diaion Polystyrene

[0108] A catalyst solution was prepared by dissolving solid  $(\text{Ind})_2\text{ZrCl}_2$  (3.37 milligrams, 8.6  $\mu\text{mol}$ ) in a solution of methyl aluminoxane (0.50 mL, type 3A, 13.1 wt.% Al and 4.69M). The catalyst mixture was stirred for 30 minutes. A 100  $\mu\text{L}$  aliquot (0.86  
20  $\mu\text{mol}$ ) was loaded onto a Diaion polystyrene bead support. The loaded catalyst was shaken until the catalyst became a free flowing powder. The catalyst (0.86  $\mu\text{mol}$ ) was placed into the bomb and injected into the 1 liter autoclave reactor via the pressurized bomb.

### Example 5

25 Slurry-Phase Ethylene-1-Hexene Copolymerization by  $\text{HN}_3\text{-Hf}$  on treated Diaion Polystyrene

[0109] A catalyst solution was prepared by dissolving  $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NHHfBz}_2$  or  $\text{HN}_3\text{-Hf}$  (12.9 milligrams, 18.4  $\mu\text{mol}$ ) in a solution of methyl aluminoxane (1.0 mL, type 3A, 13.1 wt.% Al and 4.27M). The catalyst mixture was stirred for 30  
30 minutes. A 100  $\mu\text{L}$  aliquot (1.84  $\mu\text{mol}$ ) was loaded onto a Diaion polystyrene support. The

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catalyst was shaken until it became a free flowing and powder. The catalyst mixture (1.84  $\mu\text{mol}$ ) was placed into the bomb and injected into the 1 liter autoclave reactor.

### **Example 6**

#### **5 Slurry-Phase Ethylene-1-Hexene Copolymerization by $(\text{Ind})_2\text{ZrCl}_2$ and Catalyst B on Amberchrome Polystyrene**

[0110] In a typical procedure, a catalyst solution was prepared by dissolving the  $(\text{Ind})_2\text{ZrCl}_2$  (3.37 milligrams, 8.6  $\mu\text{mol}$ ) in a solution of methyl aluminoxane (1.0 mL, type 3A, 13.1 wt.% Al and 4.27M). The catalyst mixture was stirred for 5 minutes. Another  
10 catalyst solution was prepared by dissolving solid Catalyst B (31 milligrams, 44  $\mu\text{mol}$ ) in toluene. A 0.10 mL aliquot of  $(\text{Ind})_2\text{ZrCl}_2$  catalyst was added to a 0.20 mL aliquot of catalyst B solution. The two catalyst solutions were mixed vigorously. A portion (0.15 mL, 0.86  $\mu\text{mol}$ ) of the combined catalyst solution was loaded onto Amberchrome beads (100 mg). The loaded catalyst was shaken until the catalyst became a free flowing and  
15 homogeneous powder. The catalyst mixture was placed into the bomb and injected into the 1 liter autoclave reactor.

### **Example 7**

#### **20 Results for Slurry Phase Polymerization of MAO-activated Substrates on Polystyrene Supports**

[0111] Concentrated, activated catalyst solutions were prepared by dissolution of the catalyst precursors in an alumoxane solutions (MAO) in toluene. These MAO solutions were then delivered to an appropriate quantity of the dried solid support via pipet such that the volume of liquid added was less than the total pore volume of the support material. The  
25 resulting free-flowing dry powders were then introduced to the polymerization environment as hexane slurries and the polymerization activities were determined as described in the experimental. The results are presented in Table 2 below.



**Table 2:** Slurry-phase polymerization activity of various MAO-activated substrates on polystyrene supports

Experiment	Catalyst	Support Type	Number of Runs	Activity
2	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	none	2	101519
3	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	Amberchrome	6	100502
4	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	Diaion	1	93297
5	Catalyst B	Diaion	1	39386
6	(Ind) <sub>2</sub> ZrCl <sub>2</sub> /Catalyst B	Amberchrome	7	41127

**[0112]** From the data, it can be seen that the activities of both the Amberchrom and Diaion polystyrene-supported *bis* indenylzirconium dichloride catalysts were comparable to that of the unsupported catalyst, suggesting the absence of most deleterious interactions within the support. Further, while particle morphologies are typically very poor for solution catalysts in slurry polymerization experiments, the polystyrene-supported catalyst morphologies were somewhat more granular. The addition of solid materials to slurry-phase polymerization experiments does lead to improvements in particle morphology, even when the catalyst is delivered to the reactor separately as a solution catalyst. It cannot be ascertained whether this qualitative improvement in morphology was due to predominant retention of the catalyst within the polystyrene support throughout the polymerization experiment or due to the aforementioned templating effect. Nevertheless, polystyrenic materials appear to be effective vehicles for the conveyance of liquid catalyst systems.

**[0113]** A polystyrene support was impregnated with a liquid solution of the catalyst B (Example 6). Again, the polymerization experiment verified that a solid catalyst can be prepared which possesses activity comparable to the unsupported catalyst. When a mixture of the two catalysts was prepared and absorbed into the Amberchrom material, the activity is intermediate between the two individual component activities. While the activity cannot unambiguously establish productivity from both components, SEC analysis of the resulting polymer indicates a broadened polydispersity index (PDI = 5.18) with evidence of a bimodal molecular weight distribution. This result indicates that both catalyst components contributed to the production of the polymer.

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**Example 8****Gas-Phase Ethylene Polymerization by (MeCp)Zr(CH<sub>2</sub>Ph)-triphenylcarbenium tetrakis(pentafluorophenyl)borate on treated Diaion polystyrene**

- 5   **[0114]**       A catalyst solution was prepared by dissolving (MeCp)Zr(CH<sub>2</sub>Ph)<sub>3</sub> (15.0 milligrams, 33.8 μmol) and triphenylcarbenium *tetrakis*(pentafluorophenyl)borate (30.8 mg, 33.4 μmol, 1 equiv) in a solution of fluorobenzene (1.50 mL). The catalyst mixture was stirred for 30 minutes. A 200 μL aliquot (5.41 μmol) was loaded onto Diaion polystyrene support (100mg). The loaded catalyst was shaken until the catalyst became a
- 10   free flowing and homogeneous powder. The catalyst mixture (5.41 μmol) was placed into the bomb and injected into the 1 liter autoclave reactor.

15   **Example 9**

**Gas-Phase Ethylene Polymerization by (MeCp)<sub>2</sub>Zr(CH<sub>2</sub>Ph)<sub>2</sub>-tetrakis (pentafluorophenyl) borate on Diaion Polystyrene**

- [0115]**       A catalyst solution was prepared by dissolving (MeCp)<sub>2</sub>Zr(CH<sub>2</sub>Ph)<sub>2</sub> (15.0 milligrams, 34.8 μmol) and triphenylcarbenium *tetrakis*(pentafluorophenyl)borate (30.8 mg, 33.4 μmol, 1 equiv) in fluorobenzene (1.50 mL). The catalyst mixture was stirred for
- 20   30 minutes. A 200 μL aliquot (4.64 μmol) was loaded onto Diaion polystyrene (100mg). The loaded catalyst was shaken until the catalyst became a free flowing and homogeneous powder. The catalyst mixture (4.64 μmol) was placed into the bomb and injected into the 1 liter autoclave reactor.

25

**Example 10****Gas-Phase Ethylene Polymerization by (Ind)<sub>2</sub>ZrCl<sub>2</sub> on Amberchrome Polystyrene**

- [0116]**       A catalyst solution was prepared by dissolving (Ind)<sub>2</sub>ZrCl<sub>2</sub> (3.37 milligrams, 8.6 μmol) in a solution of methyl aluminoxane (1.0 mL, type 3A, 13.1 wt.% Al and 4.27M).
- 30   The catalyst mixture was stirred for 30 minutes. A 100 μmol aliquot (0.86 μmol) was

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loaded onto an Amberchrome support (100 mg). The loaded catalyst was shaken until the catalyst became a free flowing and homogeneous powder. The catalyst mixture was placed into the bomb and injected into the 1 liter autoclave reactor.

## 5 Example 11

### Gas-Phase Ethylene Polymerization by Catalyst B on Diaion Polystyrene

[0117] A catalyst solution was prepared by dissolving Catalyst B (39.0 milligrams, 55.7  $\mu\text{mol}$ ) in a solution of methyl aluminoxane (1.00 mL, type 3A, 13.1 wt.% Al and 4.69M). The catalyst mixture was stirred for 30 minutes. A 100  $\mu\text{L}$  aliquot (5.52  $\mu\text{mol}$ ) was loaded onto a Diaion polystyrene support (100mg). The loaded catalyst was shaken until the catalyst became a free flowing and powder. The catalyst mixture (5.05  $\mu\text{mol}$ ) was placed into the bomb and injected into the 1 liter autoclave reactor.

## Example 12

### 15 Results for Gas Phase Polymerization Activity on Polystyrene

[0118] The activity of several polystyrene-supported catalysts in gas-phase experiments were determined in a stirred-bed autoclave. Catalysts containing non-coordinating anions typically are fantastically reactive species and are widely believed to be "unsupportable" on conventional silica-based supports. However, full- as well as half-sandwich zirconium borate catalyst solutions could be absorbed into Amberchrom supports and polymerize ethylene with acceptable activity; ( See Table 3).

[0119] The half-sandwich complex  $[(\text{MeCp})\text{Zr}(\text{C}_7\text{H}_7)_2][\text{B}(\text{C}_6\text{F}_5)_4]$  gave an activity of 2665 g PE  $\text{mmol}^{-1} \text{Zr h}^{-1}$  (100 psi) $^{-1}$  in a single gas-phase experiment of Example 8. Similarly,  $[(\text{MeCp})_2\text{Zr}(\text{C}_7\text{H}_7)][\text{B}(\text{C}_6\text{F}_5)_4]$  gave an activity of 1366 in a single run in Example 9. Both catalysts demonstrated kinetic behavior similar to that observed in unsupported slurry-phase experiments. The half-sandwich catalyst is much more active initially, but its activity declines in time, in contrast to the bis(cyclopentadienyl) catalyst system which appears long-lived.

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**[0120]** Prior experience has shown that evaluation of a given catalyst in a stirred-autoclave reactor operated in the gas-phase results in activities a factor of 20-50 lower than observed in slurry. It is believed that such differences are due to the lower ethylene concentration in the vapor phase coupled with the sensitivity (apparently second-order) of the polymerization rate to ethylene concentration.

**Table 3: Gas-Phase Polymerization activity  
of various substrates on polystyrene supports**

Example	Catalyst	Support Type	Number of Runs	Activity
8	$[(\text{MeCp})\text{Zr}(\text{C}_7\text{H}_7)_2][\text{B}(\text{C}_6\text{F}_5)_4]$	Diaion	1	2665
9	$[(\text{MeCp})_2\text{Zr}(\text{C}_7\text{H}_7)][\text{B}(\text{C}_6\text{F}_5)_4]$	Diaion	1	1366
10	$(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$	Amberchrom	15	1324
11	Catalyst B/MAO	Diaion	1	2874

**[0121]** The polystyrene-supported bis(indenyl)zirconium catalyst also exhibits gas-phase activity. The value reported in Table 3 represents an average of fifteen runs carried out under a variety of catalyst preparation conditions and the activities of individual runs (see Table 4, below) varied between 0 and 5300 1292 g PE mmol<sup>-1</sup> Zr h<sup>-1</sup> (100 psi)<sup>-1</sup>. These data fall in line with the activity to be expected based on the polystyrene-supported slurry-phase run. Additionally, Catalyst B showed activity in the expected range when delivered to the gas-phase on a polystyrene support.

### **Example 13**

#### **Gas-Phase Ethylene Polymerization by $(\text{Ind})_2\text{ZrCl}_2$ on Diaion Polystyrene**

**[0122]** In a typical procedure, a catalyst solution was prepared by dissolving the  $(\text{Ind})_2\text{ZrCl}_2$  (10.0 milligrams, 25.5  $\mu\text{mol}$ ) in a solution of methyl aluminoxane (1.00 mL, type 3A, 13.1 wt.% Al and 4.69M). The catalyst mixture was stirred for 30 minutes. A 100  $\mu\text{L}$  aliquot (10.11  $\mu\text{mol}$ ) was loaded onto Diaion polystyrene (100mg). The loaded catalyst was shaken until the catalyst became a free flowing and powder. The catalyst mixture (10.11  $\mu\text{mol}$ ) was placed into a bomb and injected into the 1 liter autoclave reactor.

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**Example 14****Effects of Catalyst Charge and Catalyst Loading on Vapor Phase Polymerization****Activity of Diaion PS-Supported Catalyst**

- 5 **[0123]** Data obtained in fifteen separate runs of Example 13 involving the polystyrene-supported *bis* indenylzirconium catalyst covered a wide range of catalyst preparation variables. The effects of total reactor charge and the level of catalyst loading on catalyst activity were examined. Data for the individual runs are presented in Table 4, below.

10

**Table 4:** Effects of Catalyst Charge and Catalyst Loading on Vapor Phase polymerization Activity of Diaion PS-Supported (Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO

Run	max T (°C)	Reactor charge (μmol)	mg support	Zr Loading (μmol /g)	mmol cocat.	Al/M	g PE	Activity
13-1	98.4	10.1	100	101	5.56	549	76.0	2506
13-2	95.8	10.1	100	101	5.56	549	28.3	933
13-3	96.1	5.1	100	51	2.78	550	28.7	1894
13-4	95.7	2.5	100	25	1.37	548	0.0	0
13-5	95.6	2.5	100	25	1.37	548	0.0	0
13-6	95.3	5.1	100	51	2.78	550	46.5	3069
13-7	95.5	2.5	100	25	1.37	548	4.9	980
13-8	95.9	5.1	150	34	2.78	550	7.8	772
13-9	100.5	5.1	100	51	2.78	550	54.2	5366
13-10	95.6	2.5	100	25	1.37	548	0	0
13-11	100.0	5.1	150	34	2.78	550	11.7	1158
13-12	95.2	5.1	200	25	2.78	550	0	0
13-13	98.1	5.1	175	29	2.78	550	11.4	1129
13-14	101.1	5.1	200	25	2.78	550	20.7	2050
13-15	95.4	5.1	400	13	2.78	550	0	0

**Example 15**

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**Slurry-Phase Ethylene-1-Hexene Copolymerization by (Ind)<sub>2</sub>ZrCl<sub>2</sub> on CPG 1142 Å glass beads**

[0124] A catalyst solution was prepared by dissolving (Ind)<sub>2</sub>ZrCl<sub>2</sub> (3.37 milligrams, 8.6 μmol) in a solution of methyl aluminoxane (1.0 mL, type 3A, 13.1 wt.% Al and 4.27M).

- 5 The catalyst mixture was stirred for 30 minutes. A 200 μmol aliquot (1.72 μmol) was loaded onto CPG 1142 Å glass beads (200 mg). The solid mixture was shaken until the catalyst became a free flowing and powder. A 100 mg sample (0.86 μmol) of the catalyst mixture was placed into a bomb and injected into the 1 liter autoclave reactor.

10 **Comparative Example 16**

**Slurry-Phase Ethylene-1-Hexene Copolymerization by (Ind)<sub>2</sub>ZrCl<sub>2</sub> on Davisson 958 silica**

[0125] A catalyst solution was prepared by dissolving (Ind)<sub>2</sub>ZrCl<sub>2</sub> (3.37 milligrams, 8.6 μmol) in a solution of methyl aluminoxane (1.0 mL, type 3A, 13.1 wt.% Al and 4.27M).

- 15 The catalyst mixture was stirred for 30 minutes. A 100 μL aliquot (0.86 μmol) was loaded on Davisson 958 silica support (50 mg). The loaded catalyst was shaken until the catalyst became a free flowing and homogeneous powder. The catalyst mixture was placed into a bomb and injected into the 1 liter autoclave reactor.

20 **Example 17**

**Slurry-Phase Ethylene-1-Hexene Copolymerization by (Ind)<sub>2</sub>ZrCl<sub>2</sub> on polytetrafluoroethylene**

[0126] In a typical procedure, a catalyst solution was prepared by dissolving (Ind)<sub>2</sub>ZrCl<sub>2</sub> (3.37 milligrams, 8.6 μmol) in a solution of methyl aluminoxane (1.0 mL, type 3A, 13.1 wt.% Al and 4.27M). The catalyst mixture was stirred for 30 minutes. A 100 μL aliquot (0.86 μmol) was loaded onto PTFE support (300 mg). The solid mixture was shaken until the catalyst became a free flowing and homogeneous powder. The catalyst mixture was placed into a bomb and injected into the 1 liter autoclave reactor.

30 **Example 18**

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**Gas-Phase Ethylene Polymerization by (Ind)<sub>2</sub>ZrCl<sub>2</sub> on Graphite**

[0127] In a typical example, a catalyst solution was prepared by dissolving the solid (Ind)<sub>2</sub>ZrCl<sub>2</sub> (3.37 milligrams, 8.6 μmol) in a solution of methyl aluminoxane (1.00 mL, type 3A, 13.1 wt.% Al and 4.69M). The catalyst mixture was stirred for 30 minutes. A 100 μL aliquot (0.86 μmol) was loaded onto a graphite support (200mg). The loaded catalyst was shaken until the catalyst became a free flowing and homogeneous powder. The catalyst mixture (0.86 μmol) was placed into a bomb and injected into the 1 liter autoclave reactor.

**Example 19****Slurry-Phase Ethylene Polymerization by Catalyst A on onto Diaion Polystyrene**

[0128] A catalyst solution was prepared by dissolving tetramethylbisindenylsiloxane zirconium dichloride (24.5 mg) in 1.0 mL of MAO (4.62 M solution in toluene). The catalyst mixture was stirred for 60 minutes. A 200 μL aliquot was removed and loaded onto 200 mg of controlled pore glass. The loaded catalyst was shaken until it became a free flowing and homogeneous powder and was loaded into a bomb and injected into the 1L autoclave reactor.

**Example 20****Slurry-phase Polymerization activity of Various MAO-Activated substrates on Inert Supports**

[0129] Table 5 shows the activities of bis(indenyl)zirconium dichloride catalyst absorbed into other supports of Examples 15 to 18. The activities of the catalysts absorbed into polytetrafluoroethylene were in the range of 10,000-50,000 g PE (mmol Zr)<sup>-1</sup> (100 psi)<sup>-1</sup> h<sup>-1</sup>, somewhat less than the unsupported catalyst, but clearly better than the activity of the Davisson 958 silica supported catalyst. Graphite can also be used as a vehicle for solution catalyst delivery. Four different graphitic materials were examined: granular and flaked graphites and fluorinated graphites containing high and low fluorine contents. All the graphitic materials showed acceptable activity, in the range of 47,000-54,000 g PE (mmol Zr)<sup>-1</sup> (100 psi)<sup>-1</sup> h<sup>-1</sup>, 1.5-2 times that of the silica supported catalyst system.

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**Table 5:** Slurry-phase polymerization activity of various MAO-activated substrates on inert non-styrenic supports

Example	Catalyst	Al/Zr	Support Type	Number of Runs	Activity
Comp. 2	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	none	2	101519
15	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	1142A CPG	5	74598
Comp. 16	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	958 silica	1	29959
17	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	PTFE (1 μm)	2	10814
17	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	PTFE (55 μm)	1	49248
18	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	1-2 μm graphite	2	50263
18	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	low fluorinated graphite	2	54135
18	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	high fluorinated graphite	2	47526
18	(Ind) <sub>2</sub> ZrCl <sub>2</sub>	500	flake graphite	1	48728
19	AN	200*	none	1	19833
19	AN	200	1142A CPG	3	7642

\* reference run performed with MMAO Type 3 as cocatalyst



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**CLAIMS**

We Claim:

1. A process for polymerizing olefin(s) utilizing a catalyst system, the catalyst system comprising: a polystyrene support material having an inert surface, a catalyst compound, and an activator compound.
2. The process of claim 1 wherein the catalyst compound is a bulky ligand metallocene catalyst compound.
3. The process of claim 2 wherein the bulky ligand metallocene catalyst compound is a half sandwich bulky ligand metallocene catalyst compound.
4. The process of claim 1 wherein the catalyst compound is a Group 15 containing metal catalyst compound.
5. The process of claim 1 wherein the activator compound is selected from the group consisting of methylalumoxane, modified methylalumoxane, ethylalumoxane, isobutylalumoxane, and combinations thereof.
6. The process of claim 1 wherein the activator compound is a stoichiometric activator.
7. The process of claim 1 wherein the polymerization process is a gas phase process or a slurry phase process.
8. A method of making a supported catalyst system, the method comprising the steps of:
  - a) combining a catalyst compound with an activator compound to form an activated catalyst compound; and
  - b) combining the activated catalyst compound with a polystyrene support material having an inert surface.

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9. The method of claim 8 wherein the catalyst compound is selected from the group consisting of a bulky ligand metallocene catalyst compound, a Group 15 containing metal catalyst compound, and combinations thereof.

10. The method of claim 8 wherein the activator compound is selected from the group consisting of methylalumoxane, modified methylalumoxane, ethylalumoxane, isobutylalumoxane, a stoichiometric activator compound, and combinations thereof.

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ning of each regular issue of the PCT Gazette.

(54) Title: SUPPORT MATERIALS FOR USE WITH POLYMERIZATION CATALYSTS

(57) Abstract: The invention provides new polymerization catalyst systems, including polystyrene support materials, which possesses higher activity when compared to those systems utilizing the same catalyst compound and activator supported on silica. The invention also provides methods of preparing the catalyst system, and to the catalyst system's use in a gas or slurry polymerization process.

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## INTERNATIONAL SEARCH REPORT

International Application No

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## A. CLASSIFICATION OF SUBJECT MATTER

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## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 598 543 A (MITSUBISHI PETROCHEMICAL CO) 25 May 1994 (1994-05-25) claim 7	1,2,5, 7-10
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	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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# INTERNATIONAL SEARCH REPORT

International application No.  
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## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: claims 1-10 (in part)

The subject matter of claims 1-10 (in part), insofar as it relates to metallocenes.

2. Claims: claims 1-10 (in part)

The subject matter of claims 1-10 (in part), insofar as it relates to a group 15 containing metal catalyst compound which is not a metallocene.

3. Claims: claims 1 -10 (in part)

The subject matter of claims 1-10 (in part), insofar as it relates to any other catalyst other than those defined in groups 1 or 2 above.

## INTERNATIONAL SEARCH REPORT

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